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A Computational Model for the Dimerization of Allene

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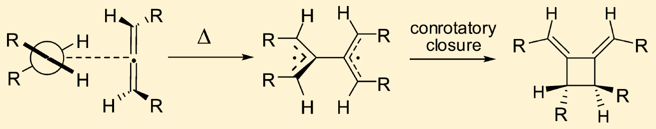
Supporting Information



ABSTRACT: Computations at the CCSD(T)/6-311+G-(d,p)//B3LYP/6-311+G(d,p) level of theory support long-held beliefs that allene dimerization to 1,2-dimethylenecyclobutane proceeds through diradical intermediates rather than a concerted ${}_{\pi}2_s + {}_{\pi}2_a$ mechanism. Two diastereomeric transition states with orthogonal and skew geometries have been located for C2−C2 dimerization of allene, with predicted barriers of 34.5 and 40.3 kcal/mol, respectively. In dimerization, the outward-facing ligands rotate in a sense opposite to the forming C−C bond. Both transition states lead to nearly orthogonal (D_2) singlet bisallyl (or tetramethyleneethane) diradical. This diradical has a barrier to planarization of 3.2 kcal/mol through a planar D_{2h} geometry and a barrier to methylene rotation of 14.3 kcal/mol. Bisallyl diradical closes through one of four degenerate paths by a conrotatory motion of the methylene groups with a predicted barrier of 15.7 kcal/mol. The low barrier to planarization of bisallyl, and similar barriers for methylene rotation and conrotatory closure are consistent with a stepwise dimerization process which can still maintain stereochemical elements of reactants. These computations support the observation that racemic 1,3-disubstituted allenes, with access to an orthogonal transition state which minimizes steric strain, will dimerize more readily than enantiopure materials and by a mechanism that preferentially bonds M and P enantiomers.

■ INTRODUCTION

Allene (**1**) and its derivatives undergo facile thermal dimerization (Scheme 1) to afford primarily 1,2-dimethylenecyclobutanes (**3**).[1] The parent reaction was first described by Lebedev in 1913[2] and later shown by other groups to produce a small percentage of isomeric dimer 1,3-dimethylenecyclobutane (**4**), as well as trimers that suggest trapping of an intermediate diradical.[3] Dolbier reported yields of **3** up to 95% when dilute solutions of allene in benzene are heated at 130−200 °C.[4] Christl has cited activation parameters[5] of $\Delta H^{\ddagger} = 26.9$ kcal/mol and $\Delta S^{\ddagger} = -25.9$ cal mol^{-1} K^{-1} based on unpublished results from gas phase studies of Roth and Schaffers.[6] Most other allenes show similar behavior upon heating.[1] Jacobs showed that 1,3-diadamantylallene does not dimerize but instead yields products from a diradical intermediate.[7] For strained cyclic allenes, dimerization usually prevents isolation,[8] although steric effects can hinder bimolecular reaction. 1,2-Cyclooctadiene dimerizes at room temperature,[9] but we have shown that the 1-*tert*-butyl derivative is isolable.[10] Allene dimerizations and closely related 2 + 2 cycloadditions to alkenes have found application in the synthesis of cyclobutane rings and more complex substances.[1a,b,11]

Scheme 1 outlines mechanistic alternatives for dimerization of allene. A concerted ${}_{\pi}2_s + {}_{\pi}2_a$ mechanism (**TS2**) is possible according to orbital symmetry and might produce either **3** or **4**.[12] Pasto has argued for concerted dimerization of allenes through an unusual six-electron transition state.[13] In spite of these arguments, a preponderance of experimental evidence with different types of allenes over many decades has supported a stepwise dimerization mechanism that proceeds through a singlet bis-allyl diradical such as **6S**.[1a,b,4b,5,7,11h,14] Dolbier reported a negligible secondary deuterium isotope effect in the dimerization of tetradeuterioallene ($k_H/k_D = 1.013 \pm 0.020$) but a larger effect ($k_H/k_D = 1.14 \pm 0.020$) with dideuterioallene, concluding that a two-step mechanism must be operative.[4] This would have two distinct transition states, one for initial C2−C2 bond formation and the second for closure to diene **3**. Perhaps the most convincing experiment in support of a diradical intermediate was Levek and Kiefer's report that dimerization of 1,1-dimethylallene and pyrolysis of an azo-precursor to the expected diradical both afforded identical product mixtures.[14d] The alternative C1−C2 stepwise dimerization, also expected to be stepwise, is known to be a very minor pathway,[3] presumably because diradical **9S** with a vinyl radical component should lie at much higher energy that **6S**. A third stepwise route through initial C1−C1 bonding must be at still higher energy and is not considered here.

The most likely diradical intermediate in this reaction, commonly known as bisallyl or tetramethyleneethane (TME), has been well studied because of its unusual disjoint[15] electronic structure.[16] The singlet (**6S**) and triplet electronic states of bisallyl are nearly degenerate; after some years of disagreement, the best current computational and experimental results support a singlet ground state with an orthogonal geometry.[16] Hoffmann enumerated potential products from **6S** and concluded that both disrotatory and conrotatory paths may exist for closure to **3**.[17] The reverse reaction in which **3** and simple derivatives rearrange through reversible ring-opening to diradical **6S** had been studied by several groups.[18−20] Hoffmann noted that a concerted Cope rearrangement is possible for **3**,[17] but the geometry probably precludes this process. Doering and

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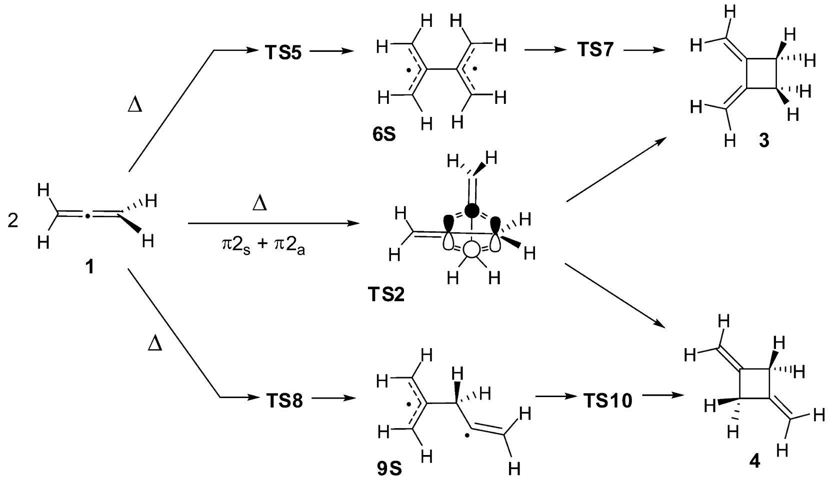
Scheme 1. Mechanisms for Allene Dimerization



Dolbier reported an activation energy of 46.8 kcal/mol for ring-opening of **3** and they favored **6S** as an intermediate.[19] Using alkyl substituents, Gajewski and co-workers provided clear evidence that initial ring-opening of **3** is conrotatory;[20b] microscopic reversibility implies that the closure of **6S** to **3** should favor the same stereochemistry. The same authors showed that bisallyl must undergo facile rotation about the central bond.[20a,c−e]

This stepwise diradical mechanism does not preclude regioselective or stereospecific product formation. Based on the observation that enantiomerically pure and racemic 1,2-cyclononadiene give different ratios of [2 + 2] dimeric products, Moore and co-workers concluded in 1969, "...we suggest that in general one must consider the possibility that intermediates both appear and react stereospecifically."[14i] Christl reported a similar observation for 1,3-diphenylallene, even though products were racemic.[5] In the dimerization of 1-phenyl-1,2-cyclooctadiene, the same author noted that, "...pairs of enantiomers react 38 times faster than pairs of homomers" and presented a detailed scheme for allene dimerization.[5] These results seem paradoxical: how can a stepwise diradical mechanism proceed with a high level of selectivity and stereospecificity? This same problem has been faced with other stereochemically complex processes such as the vinylcyclopropane to cyclopentene rearrangement.[21]

It is surprising that this long-accepted diradical mechanism for allene dimerization and its connection with the interconversion of diradical **6S** and **3** have not yet been examined in detail by theory. Only rudimentary computational models for the dimerization of allene have been presented. The most recent CNDO/2 computations three decades ago[22] support a diradical mechanism for allene dimerization, but this level of theory cannot provide accurate predictions on such an electronically complex process. We describe here the results of CCSD(T)//DFT models on dimerization of allene and the ring-opening of **3**. Our goal in the present work is to understand the essential reaction mechanism and stereochemistry of allene cycloadditions.

COMPUTATIONAL METHODOLOGY

All calculations were carried out with Gaussian 09[23] or Spartan 10.[24] Structures were optimized and characterized by frequency analysis at the (U)B3LYP/6-311+G(d,p) level of theory, followed by single-point (U)CCSD(T)/6-311+G(d,p) calculation. For dimerization and ring-closure transition states, the intrinsic reaction coordinate (IRC) was calculated to verify connection with reactants or product. A "broken-symmetry" guess was used for open shell singlet DFT and CCSD(T) calculations, with care to use the same unbiased guess for each point on the DFT IRC. To arrive at the best estimates of reaction energetics, unscaled DFT zero-point vibrational energy (ZPVE) corrections have been applied to both DFT and CCSD(T) energies.

RESULTS AND DISCUSSION

The main computational results of this study are summarized in Figure 1, which shows CCSD(T) energetics at DFT-optimized geometries. Figure 2 presents optimized geometries for stationary points, while Table 1 gives a compilation of DFT and CCSD(T)//DFT energetics. Both energies include DFT zero- point corrections.

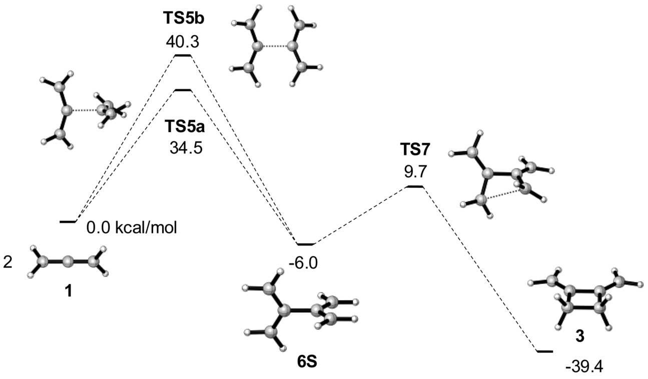


Figure 1. CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) energetics of allene dimerization.

Our analysis suggested that *two* diastereomeric transition states should exist, even for dimerization of the parent allene. This occurs because, when allene is bent, the ligands twist synchronously to a chiral C_2 geometry[25] and thus two diastereomeric modes of approach are possible, which bond bent allenes of different helicity.

Optimization of trial structures corresponding to this analysis yielded the predicted diastereomeric transition states for allene dimerization: **TS5a** (orthogonal, D_2 symmetry) and **TS5b**

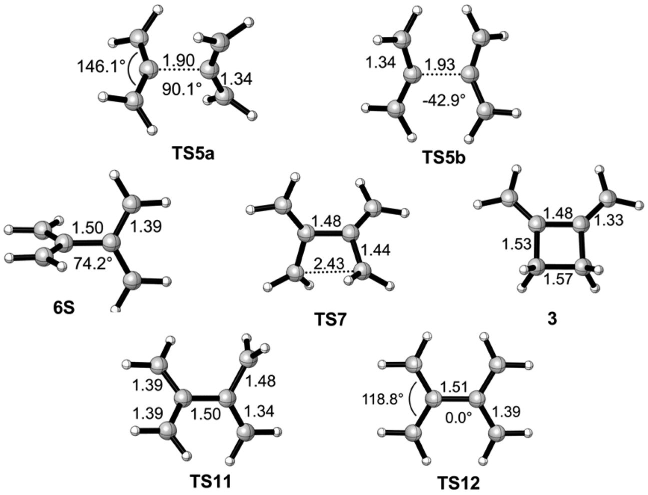


Figure 2. B3LYP/6-311+G(d,p)-optimized structures (bond lengths in angstroms).

Table 1. DFT and CCSD(T) Relative Energies (kcal/mol)

structure	E_{rel} DFT[a]	E_{rel}(CCSD(T))[b]
allene (**1**) x 2	0.00	0.00
TS5a (D_2)	32.9	34.5
TS5b (C_2)	38.3	40.3
6S (D_2)	0.19	−6.0
TS7	15.2	9.7
3	−29.2	−39.4
TS11	16.0	8.6
TS12	2.03	−2.50
TS8	40.3	41.5
9S	23.3	16.8
TS10	28.0	22.3
4	−26.5	−37.3

[a](U)B3LYP/6-311+G(d,p) + ZPVE. [b]CCSD(T)/6-311+G(d,p)//B3LYP + ZPVE.

(skew, C_2 symmetry). According to the IRCs, each dimerization follows a different path but arrives at the same diradical intermediate **6S**. In the lower energy transition state **TS5a**, the two allenes approach in an orthogonal geometry of D_2 symmetry and remain nearly orthogonal all the way to diradical **6S**. The structure remains closed shell (B3LYP, $S^2 = 0$) up to transition state **TS5a** but gradually transforms into the singlet diradical beyond this point. The skew transition state **TS5b** maintains C_2 symmetry with a twist angle of ca. 42°. **TS5b** lies 5.8 kcal/mol higher in energy than **TS5a**; this is clearly a consequence of closer approach of the inner hydrogen pairs. According to the IRC plots, the synchrony of methylene rotations is similar for both cases. Four hydrogens which are oriented away from the structure in the initial approach rotate outward as the C2−C2 bond forms. Methylene rotation continues in the same direction beyond the transition states. This step leading to **6S** is only modestly exothermic.

All efforts to locate a first-order concerted ${}_{\pi}2_s + {}_{\pi}2_a$ transition-state structure **TS2** failed; if **TS2** exists, it is certainly at higher energy. Trial geometries invariably optimized to **TS5a** which is also closed shell. Our prediction for the energetics of allene dimerization to **3** (−39.4 kcal/mol) is very close to the value of −36.9 kcal/mol which may be estimated from NIST heats of formation. This is about twice the exothermicity of ethyene dimerization and reflects the inherent thermodynamic instability of allene. There is a good correspondence (Table 1) between DFT and CCSD(T) energetics. However, our predicted DFT or CCSD(T) activation energies are significantly higher than the value cited by Christl.[5]

The highest level computations on singlet diradical **6S** have predicted an orthogonal geometry with a low barrier to rotation about the central C−C bond.[16] We find that DFT methods yield D_2 symmetric geometries which are close to orthogonal; for example, UB3LYP/6-311+G(d,p) and Truhlar[26] UM05-2X/6-311+G(d,p) optimizations predict geometries with dihedral angles of 74° and 48°, respectively. Scanning the rotational potential surface (Supporting Information, Figure S1) shows a broad, nearly flat region from ca. 60 to 90°. Diradical **6S** has multiple degenerate modes of closure to diene **3**. The least motion paths from **6S** are best described as conrotatory with respect to methylene group rotation and this is exactly what is shown by the IRC for this process (Supporting Information, Figure S4). The barrier to closure is predicted to be 15.7 kcal/mol. Not surprisingly, our attempts to locate a first-order disrotatory transition state failed.

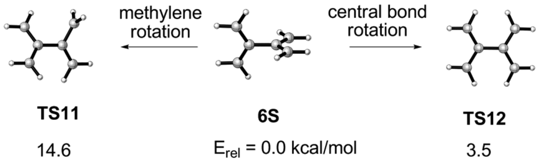


Figure 3. Rotational barriers in the singlet bis-allyl diradical (UCCSD(T)//B3LYP + ZPVE).

As two allenes dimerize, chirality may be lost through formation of an achiral diradical; however, as described above, rotation of the ligands will be stereospecific. If the diradical retains reactant stereochemistry, conrotatory closure can then result in stereospecific product formation. Thus, two additional reaction channels for the diradical are important. The predicted barrier to central bond rotation in **6S** through a D_{2h} structure (Figure 3, **TS12**) is 3.5 kcal/mol. This process planarizes the allene, providing an easy route to racemization in the dimerization of chiral allenes. Also of significance is rotation about one of the methylene carbons, for which we estimate a barrier (**TS11**) of 14.6 kcal/mol. For diradical **6S**, barriers for methylene rotation (**TS11**) and conrotatory closure (**TS7**; 15.7 kcal/mol) are thus similar in magnitude. These results are consistent with a dimerization process which passes through a diradical intermediate and may even lead to racemization but still can maintain stereochemical elements of reactants. The stereospecific dimerization of some allenes suggests that dynamic control may be operative, favoring ring closure over methylene rotation.

For the reverse process, ring-opening of **3**, Doering[19b] and Gajewski[20a] independently demonstrated a diradical intermediate, presumed to be **6S**, by showing that hydrogen and deuterium labels are scrambled. Gajewski later presented evidence for stereospecific conrotatory opening.[20b] Doering reported an activation energy of 46.8 kcal/mol.[19b] Our CCSD(T)//DFT computations predict a barrier of 49.1 kcal/mol for conrotatory reaction, in good agreement with these experimental results. No first-order disrotatory transition state could be found for ring-opening.

CCSD(T)/B3LYP energetics for the alternate dimerization pathway from **1** to **4** are summarized in Figure 4. The initial barrier is too large for this to be competitive with C2−C2

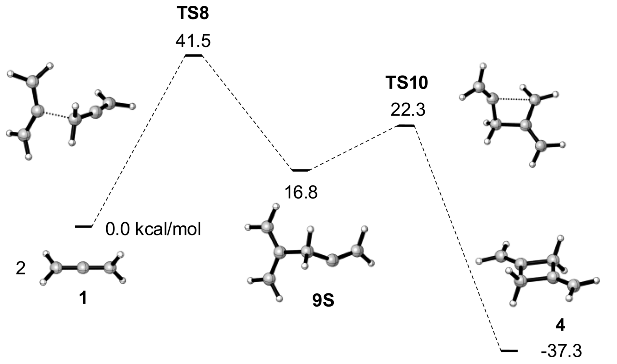


Figure 4. C1−C2 dimerization pathway (CCSD(T)//B3LYP + ZPVE).

dimerization. This is a consequence of the diminished stability of diradical **9S**, which has both allyl and vinyl radical character.

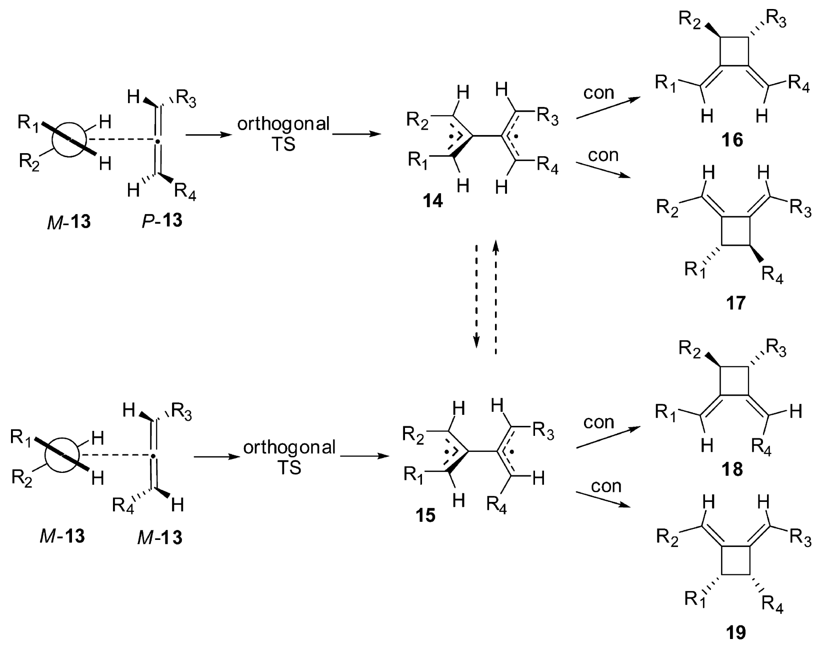
Scheme 2 presents a simple description of the stereochemistry of allene dimerization that combine's Christl's insightful analysis[5] with results from the present computations. Although two transition states exist, it is likely that both M + M and M + P allene pairs will access the lower energy orthogonal TS similar to **TS5a**, but with different consequences. For the M + P pair, ligands R_1 through R_4 approach anti to the forming C2−C2 bond and rotate outward, leading directly to diradical **14**. This process minimizes steric interaction among the ligands. By contrast, with a homochiral M + M (or P + P) pair, one ligand (R_4) must point inward as C2−C2 bonding proceeds to form stereoisomeric diradical **15**. The differences in steric strain due to orientation of this one ligand explain why M + P allene pairs should react faster than M + M or P + P pairs. This is consistent with experiment.[5] It is noteworthy that a similar prediction has been made for alkenes. In their classic treatise on orbital symmetry, Woodward and Hoffmann noted that thermal $_{\pi}2_s$ + $_{\pi}2_a$ dimerization of chiral cyclic alkenes should favor reaction of enantiomeric pairs, thus "...optically active forms of the olefins... will dimerize less readily than the racemic substances."[12]

In the second step of this process, conrotatory closure of diradicals **14** or **15** should have different outcomes. Closure of **14** in either direction produces *trans* stereochemistry on the four-membered ring to yield **16** or **17** which have the same stereochemistry. By contrast, **15** can close in two directions to give stereoisomers**18** or **19**. This analysis is in excellent agreement with experimental results reported for 1,3-diphenylallene.[5] Cyclic allenes follow similar pathways. Enantiomerically pure 1,2-cyclononadiene favors a cis-dimer similar to **19**, while racemic material gives primarily a trans dimer similar to **16**. In each case, racemization is assured due to an achiral intermediate and facile rotation about the central bond, while interconversion of **14** and **15** is minimized because of the significant barrier to rotation. Reaction dynamics may also favor conrotatory closure (**TS7**) over methylene group rotation (**TS11**).

■ SUMMARY AND CONCLUSIONS

Results presented here support long-held beliefs that dimerization of allene should proceed through diradical intermediates, rather than a concerted $_{\pi}2_s$ + $_{\pi}2_a$ mechanism. Two diastereomeric transition states are predicted by our calculations. The lower energy reaction path through **TS5a** begins by orthogonal approach of two allenes (Figure 1) that bond at their central atoms through an orthogonal D_2 geometry (S_4 symmetry at precisely 90°) with a barrier estimated to be 34.4 kcal/mol. A skew transition state **TS5b** with C_2 symmetry is located nearly 6 kcal/mol higher and seems likely to play a minimal role in allene dimerizations. Both C2−C2 dimerization transition states lead to the bisallyl diradical **6S** by stereospecific paths in which the outward-facing ligands rotate in a sense opposite to the forming C−C bond. The small barrier to planarization (**TS12**) of **6S** and similarity of barriers for methylene rotation (**TS11**) and conrotatory closure (**TS7**) are consistent with a stepwise dimerization process which can still maintain stereochemical elements of reactants. This occurs

Scheme 2. Stereochemistry of Allene Dimerization



because pathways to and from the diradical intermediate **6S** are stereospecific. Our computations support the observation that racemic 1,3-disubstituted allenes, with access to a transition state which minimizes steric strain, will dimerize more readily than enantiopure materials and by a mechanism that bonds M and P enantiomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Intrinsic reaction coordinate plots, Cartesian coordinates, and energies for stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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